APR 5 1926

61–4

Proceedings of the American Academy of Arts and Sciences.

Vol. 61. No. 4. February, 1926.

THERMAL CONDUCTIVITY AND THERMAL E.M.F. OF SINGLE CRYSTALS OF SEVERAL NON-CUBIC METALS.

By P. W. Bridgman.

This research was carried on under a grant from the Rumford fund and the cost of publication has been met from the Rumford fund.

(Continued from page 3 of cover.)

VOLUME 61.

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Presented October 14, 1925. Received November 16, 1925.

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Introduction.

In this paper previous investigations of the properties of several metals crystallizing in non-cubic systems[1] are extended to thermal conductivity and thermal e.m.f. The thermal conductivity is measured at room temperature and the thermal e.m.f. in the range between room temperature and 100° C. Fairly complete results are presented here for Zn, Cd, and Sn in all possible orientations in the crystal and for Bi over a restricted range of orientations, whereas for Sb and Te only measurements of thermal e.m.f. have been obtained and only for those orientations in which the cleavage plane is nearly parallel to the length. The mechanical difficulty of obtaining suitable specimens of the proper orientations is responsible for the lack of completeness.

Apart from the exact numerical results, there are several interesting questions involved in the data presented here. With regard to thermal conductivity we have to ask whether the symmetry relations deduced by Voigt hold, and also whether the Wiedemann-Franz proportionality between electrical resistance and thermal conductivity holds in detail for all directions in the crystal. It will appear that the symmetry relations of Voigt do hold, but that the Wiedemann-Franz ratio does not hold in detail. With regard to the thermo-electric effects, we have to discuss the Thomson heat and the Peltier heat. It will appear that the analysis of Voigt considers only the Thomson heat, the Peltier heat at surfaces of discontinuity, which is numerically by far the more important effect, having been completely neglected. It is probable that the symmetry relations of Voigt apply to the Thomson heat, but that the symmetry relations of the Peltier heat are different. It is shown in the discussion that a Peltier heat varying with the orientation in the crystal involves an internal Peltier heat when the direction of current flow in the crystal changes.

Part I. Thermal Conductivity.

Method of Measuring Thermal Conductivity.

The methods available were much restricted by the requirement that the parts of the crystal subjected to measurement should not be subjected to any machining operation. Previous work with single crystals[1] has shown the very great difficulty of machining without seriously upsetting the crystal structure. The general scheme of the method adopted was as direct as possible; the temperature difference between two points at a known distance apart on a rod was measured when a known heat current passes along the rod. The heat current was produced electrically by a heating coil attached to one end of the rod, the other end of the rod being maintained at constant temperature in a temperature bath and so acting as a sink. The temperature difference was measured by a differential thermo-couple attached to the rod at intermediate points.

The experimental arrangements for measuring the thermal conductivity are shown in Figure 1. The metal is a unicrystalline casting, *A*, made by methods already fully described,[2] about 10 cm. long and very nearly 6 mm. in diameter. It is mounted by soldering with low melting solder into the massive copper block *B*. A special jig used during the setting of the solder ensured that the rod was central in the block. The heating coil *C* at the upper end was contained in a

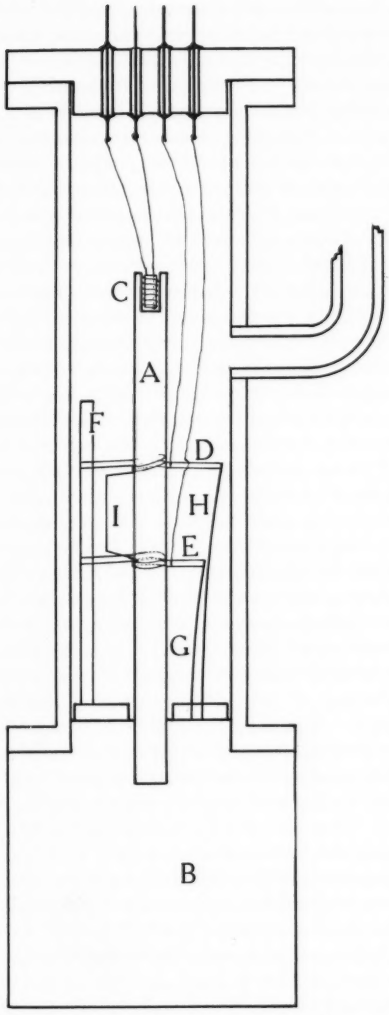

FIGURE 1. Section of apparatus for measuring thermal conductivity.

recess, 3.3 mm. in diameter and 6 mm. deep, drilled into the rod. Any damage to the crystal structure in drilling the hole was confined to the immediate neighborhood of the hole, and could not affect the lines of heat flow near the thermo-couples. The heating coil was of high resistance wire 0.009 cm. in diameter, wound in a thread cut in a miniature cylinder of pipestone, the total resistance being about 35 ohms. The coil was insulated externally with a wrapping of paper 0.0025 cm. thick; before an experiment the insulation resistance between coil and rod was checked and required to be over 10^8 ohms. The leads to the heating coil were of copper 0.013 cm. in diameter. To insure good thermal contact between coil and rod the hole in the upper end of the rod was filled with vaseline before inserting the coil, and the excess vaseline was afterward wiped away.

The thermo-couple was of copper-constantan ribbon, made by rolling to a thickness of less than 0.0025 cm. wire originally 0.015 cm. thick. The couple was held in contact with the rod with springs. The details of construction of the couple were as follows: Two ribbons of copper, *D* and *E*, attached at one end by soldered loops to the insulating pillar *F*, were passed once around the rod, and at the other ends were held taut by the piano wire springs *G* and *H* from which they were insulated by glass sleeves. Underneath the two loops of copper was passed the constantan ribbon *I*, which was then soldered to the copper with the minimum amount of solder. As shown in the figure, the constantan ribbon was bent at right angles to the rod where it made contact with the copper. Copper connections 0.012 cm. in diameter, soldered to the ribbons *D* and *E* near the rod, led to a potentiometer and provided means of measuring the potential difference and so the difference of temperature between the two ends of the constantan ribbon. The thermo-couple was insulated from the rod by a single wrapping of oiled paper 0.0025 cm. thick, stuck to the rod with a very thin coating of air drying lacquer. The insulation resistance between couple and rod was always required to be greater than 10^8 ohms. To ensure better thermal contact between rod and couple the loop around the rod was painted with lacquer above the paper after assembling. The distance between the junctions constantan to copper was read for each specimen with a telescope mounted on a comparator, and was always nearly 2 cm.

The springs holding the thermo-couple taut were so mounted that they could be slacked after a run, and the crystal rod slipped out through the loosened loops. The couple could conversely be slipped over a freshly mounted rod and the loops tightened into place. Simi-

larly the heating coil at the upper end was removable from specimen to specimen. All the measurements on thermal conductivity on all the specimens were made with the same thermo-couple and same heating coil, and for all except Bi with the same heat input, so that all the results are comparable, apart from any question of absolute values.

The rod with the thermo-couple attached was placed inside a brass cylinder 3 cm. in inside diameter and 20 cm. long. This cylinder was provided with flanges at the top and bottom by which vacuum tight connection was made to the copper block *B* and to a brass plate at the upper end through which passed terminals for the thermo-couple and the heating coil insulated with glass tubing and deKhotinski cement. Connection to the vacuum pump was made with a brass tube soldered into the side of the cylinder. The vacuum was produced with a mercury diffusion pump with the conventional fore-pumps. There was provision for a liquid air trap, but this was never used. Trial showed no difference in the results when the trap was packed in ice or when left at room temperature. Since this difference of temperature corresponds to a difference of vapor pressure of the mercury of about eight fold, it was concluded that the heat dissipated by convection or conduction by the gas surrounding the rod was negligible, and that the diffusion pump vacuum at ordinary temperatures was sufficient. The importance of the vacuum became at once obvious if one attempted readings at full atmospheric pressure. Here there were fluctuations so violent that no consistent readings could be obtained; what rough readings could be obtained indicated a conductivity materially higher than given with the vacuum, showing that an appreciable part of the heat input was carried away by the gas at atmospheric pressure.

The electrical measurements do not need detailed description The thermal e.m.f. of the couple and the heating current were both measured with the same potentiometer that was previously used in measuring the effect of pressure on the thermal conductivity of metals,[3] and a full description will be found in that paper. The heating current was provided by a storage battery of 12 volts in series with appropriate resistances and a ballast lamp to maintain constancy. The maximum heating current was about 0.4 amp. The sensitiveness of the measurements was very much better than 0.1%, and very much better than the consistency of the measurements with different specimens.

The experimental procedure was as follows: The rod was soldered into the copper block *B*, paper strips 6 mm. wide were lacquered on at

the mean position of the thermo-couples, the thermo-couples adjusted, the heating coil inserted, soldered connection made between the couple and the heating coil leads and the fixed copper terminals in the upper brass plate, clamps applied to the flanges to make them vacuum tight (the conventional vacuum wax was used underneath the flanges), the assembly was then placed in the temperature bath of water at room temperature with the upper brass plate projecting a couple of cm. above the surface of the water, connections were made to the vacuum pump through a conical joint between glass and brass sealed in deKhotinski cement (the diffusion pump and the brass assembly were slung from counterpoised arms to allow free relative motion), the insulation resistance was tested between the thermocouple and the heating coil and the grounded rod, soldered connection made between the outer terminals in the upper brass plate and the potentiometer and the source of heating current, and the vacuum pump and heating current started. The vacuum was tested by noting the character of the discharge through a small discharge tube excited by a transformer on the commercial 60 cycle 110 volt circuit. No final readings were made until ½ hour had elapsed after the last previous change of heating current, this interval having been proved sufficient by trial, and after reaching a vacuum so high that all discharge had ceased. Readings were made for two different heat inputs, one about 4 times the other; the readings with the smaller heat input were made first and were merely by way of check. These were sometimes made before complete equilibrium was reached. In general the conductivity calculated from the small heat input was a few per cent higher than that with the larger input; the results with the larger input are to be preferred, and are the only ones retained in the final results.

Detailed Results.

The theoretical connection between thermal conductivity and direction in the crystal has been worked out by Voigt; the connection is the same as for the electrical conductivity. This means that for the crystals investigated here, which have rotational symmetry, the behavior of the conductivity in all directions is completely characterized by two constants. These two constants are the thermal conductivity parallel and perpendicular to the axis of rotational symmetry. Denote these conductivities by κ_{11} and $\kappa_{\perp}$, and introduce the reciprocal conductivity or thermal resistance, namely

$$\lambda_{11} = \frac{1}{\kappa_{11}}, \quad \text{and} \quad \lambda_{\perp} = \frac{1}{\kappa_{\perp}}.$$

The relation of Voigt is now

$$\lambda_\theta = \lambda_\perp + (\lambda_{11} - \lambda_\perp) \cos^2 \theta,$$

where λ_θ denotes the reciprocal conductivity in the direction inclined at the angle θ to the axis. The relation for electrical resistance is the same, namely

$$\rho_\theta = \rho_\perp + (\rho_{11} - \rho_\perp) \cos^2 \theta.$$

Now eliminate θ between the equations, giving

$$\lambda_\theta = \frac{\rho_\theta(\lambda_{11} - \lambda_\perp) + \rho_{11}\lambda_\perp - \rho_\perp\lambda_{11}}{\rho_{11} - \rho_\perp}.$$

Hence λ_θ is a linear function of ρ_θ, in virtue merely of the symmetry relations, and without any special hypothesis connecting electrical and thermal conductivity.

One of the points of chief interest in this investigation of thermal conductivity is whether the Wiedemann-Franz ratio continues to hold for the individual directions in a crystal. If this is the case, λ in any direction is proportional to ρ in that direction, which is at once seen to be consistent with the equation above, for on putting $\lambda_{11} = \alpha\rho_{11}$, and $\lambda_\perp = \alpha\rho_\perp$, the equation collapses to

$$\lambda_\theta = \alpha\rho_\theta.$$

Hence if the Wiedemann-Franz ratio holds for all directions, not only is λ_θ a linear function of ρ_θ, but the straight line passes through the origin. In the following this criterion is applied graphically to the thermal resistance.

In computing the results, the data needed are the heat input, given by the heating current and resistance of the heating coil, the temperature difference, given by the thermal e.m.f. of the couple and the constant of the couple, the cross section of the rod, and the distance between the junctions of the thermo-couple. In terms of all these data the absolute thermal conductivity can be at once obtained, provided that heat losses be neglected. The heat losses are of two kinds; losses by radiation or by convection and conduction through the small amount of gas remaining, and loss by conduction along the leads of the heating coil or an effective loss by conduction along the wires of the thermo-couple. The precise amount of these various losses would be difficult to determine experimentally; calculation shows most of them to be very small, and direct experiment by varying the gas pressure showed that loss through the gas must be small. In the calculation of conductivity such losses were entirely neglected,

and it must be recognized that there is here a possible source of error. The heating was so small that the rise of temperature above the surroundings at the heating coil end of the rod was only 2° for Sn, less for Zn and Cd, and not over 7.5° in the extreme case of Bi. The heat loss should be proportional to the temperature rise and therefore inversely proportional to the thermal conductivity. There is another possible source of error in the value of the constant assumed for the thermo-couple. It would have been difficult to calibrate the couple directly, and the value (100×10^{-6} volts = 2.48° C.) given by L. H. Adams[4] in his Table for copper—"Ideal" was assumed. It is questionable, however, whether the very great mechanical deformation involved in rolling the wire flat (it was not annealed afterward) may not have seriously affected the constant. However, since all specimens were measured with the same couple, any error in the constant can produce no error in the relative conductivities of the various samples, and can have no effect on any conclusions made as to connections between electrical and thermal conductivity. The absolute thermal conductivities calculated, neglecting heat losses and with the assumed value for the thermo-couple constant, are uniformly too high to be consistent with the values given in the literature for cast rods in which the crystal grains are at haphazard. The inconsistency amounts to about 20% for Cd, Zn, and Sn, and for Bi to about two fold. I do not believe that nearly all of this discrepancy can be due to the factors discussed (heat leak and constant of the couple) but that an important part must be real, which means that the thermal conductivity in my single crystals is high, arising perhaps from a combination of unusual purity with a perfectly regular atomic arrangement. It is to be expected that this effect will be particularly large in Bi, in which the crystalline character is most pronounced, and cleavage most easy.

The Specimens. The rods were cast and examined to ensure that they contained only one crystal grain by methods already described.[1] A simple method of controlling the orientation of the crystalline axis with respect to the axis of the rod has not yet been developed, and I did as before, selecting those best oriented from a number of castings. Because of the small diameter of the casting, only 6 mm., large angles of inclination between the axis of the crystal and the casting were more common than in the larger size castings.

Zinc was Kahlbaum's best; measurements were made on 8 rods, of angles varying from 86.5° to 33°. The angle was determined from the position of the cleavage plane.

Bismuth was electrolytic metal from the U. S. Metals Refining Co., the same as the Bi of the previous measurements. Before casting into the 6 mm. rods it had been cast by the regular procedure for making unicrystalline castings into rods 2.5 cm. in diameter. These were not one grain. The lower part of these rods, which thus had experienced an additional purification, was used for the 6 mm. rods. In the previous paper it was mentioned that it is particularly hard to get Bi in unicrystalline rods, there being a very strong tendency to form several grains of very nearly the same orientation. This difficulty was again found in high degree, and in many trials only a few satisfactory rods, of angles varying from 90° to 68.5° were obtained. Since these measurements were completed, however, a much better method has been developed for obtaining unicrystalline rods of Bi. The difficulty is apparently connected with the expansion on solidifying. The crystal that separates in the bottom of the container is lighter than the liquid and is therefore mechanically unstable. Portions of the crystal tend to detach themselves after being laid down, and act as new centers of crystallization. This tendency may in large part be avoided by drawing the mold up through the top of the furnace instead of lowering through the bottom, so that the Bi crystal is in a mechanically stable position at the top.

The angle between the axis of the casting and the crystal for these Bi rods was determined from the cleavage plane.

Cadmium was Kahlbaum's best; successful measurements were made on 9 rods. The singleness of the castings was determined in the regular way by the appearance of the castings in reflected light. There was a difficulty not met before, however, in determining from the reflection pattern the location of the crystal axis, since for some reason under these special conditions not all the faces of the reflection pattern were developed. It turned out to be much simpler to obtain the location of the axis from measurement of the specific electrical resistance, the specific resistance parallel to and perpendicular to the axis having been previously determined. In measuring the resistance the apparatus of the previous paper was used. The values found for the specfic resistance varied from 6.92×10^{-6} to 8.31, the previous values for $\rho_{\perp}$ and ρ_{11} being respectively 6.80 and 8.30. It thus appears that the 9 rods used ranged through nearly all the possible orientations.

Tin was measured in 5 specimens; 3 of these were Bureau of Standards melting point samples, and 2 were Kahlbaum's purest. Again, although the reflection patterns were sufficiently developed to determine the uniqueness of the grains, all the faces were not present, so

that the orientation of the axis had to be determined from the specific electrical resistance. This ranged from 9.92×10^{-6} to 13.20; the previous values are $\rho_1 = 9.9$, $\rho_{11} = 14.3 \times 10^{-6}$, so that about two-thirds of the total possible range of orientations is here represented.

Numerical Results. The accuracy of the results is so low that graphical representation is adequate. In Figure 2 is plotted for all

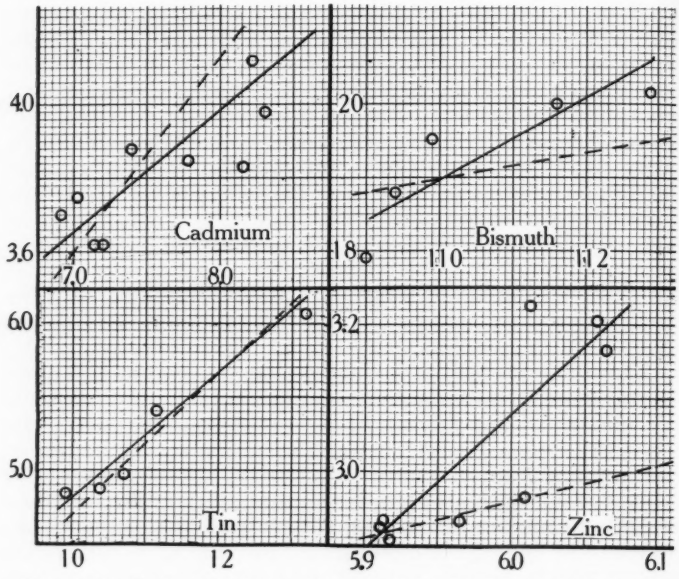

FIGURE 2. Reciprocal of thermal conductivity (ordinate) against specific resistance $\times 10^6$ (abscissa).

the metals the reciprocal of thermal conductivity (calculated as explained) against specific electrical resistance of the same sample. According to the symmetry relations developed by Voigt[5] the relation between these two should be linear. The heavy lines in the diagrams appear to be the best straight lines connecting the observed points. The experimental error is seen to be considerable. If, further, the Wiedemann-Franz ratio holds for the individual directions in a crystal, the straight line should pass through the origin. The dotted lines in the diagrams are the best lines drawn through the origin.

In the case of Sn and perhaps in that of Bi, this line connecting with the origin may also within experimental error be the line on which the points actually lie, so that for Sn and possibly for Bi the proportionality between electrical and thermal resistance holds for different directions in a single crystal. It has already been found by Kaye and Roberts[5a] that in Bi the ratio of the thermal conductivities in the perpendicular and parallel directions is 1.39, which is to be compared with my value[1] 1.27 for the ratio of the electrical conductivities. The discrepancy is in the same direction as indicated in Fig. 2.

But with Cd and Zn there seems no room for doubt that the experimental points do not lie within experimental error on the line through the origin, so that for these metals the Wiedemann-Franz proportionality does not hold in detail for different directions in the crystal. In the case of cadmium, electrical resistance varies more with direction than thermal conductivity, and for Zinc thermal conductivity varies more than electrical resistance. It would seem that these conclusions cannot be affected by any uncertainties in the values given for the absolute conductivities.

Whether or not the Wiedemann-Franz ratio holds, it is evident that for all four metals the electrical conductivity increases in the same direction in which the thermal conductivity increases.

Part II. Thermal E.M.F.

Methods of Measuring Thermal E. M. F.

The single crystal rods on which the thermal e.m.f. measurements were made were 6 mm. in diameter and about 15 cm. long. In point of time the thermal e.m.f. measurements were made before the measurements of thermal conductivity; after the thermal e.m.f. measurements some of the rods were selected for the measurements of thermal conductivity, being cut down to 10 cm. in length. The number of specimens used was as follows. Zn, 8 thermal e.m.f. specimens were measured and all 8 were again used for thermal conductivity; Sn, 14 thermal e.m.f. specimens were used from which 5 were selected for thermal conductivity; Cd, there were 14 thermal e.m.f. specimens from which 9 were selected for thermal conductivity; Bi, there were 10 thermal e.m.f. specimens of which 5 were used for thermal conductivity; Sb, there was only 1 thermal e.m.f. specimen which was not suitable for thermal conductivity; Te, there were 3 thermal e.m.f. specimens of which none were suitable for thermal con-

ductivity. With regard to Sb and Te it is to be noticed that geometrical imperfections are not a source of inaccuracy in measurements of thermal e.m.f., whereas geometrical perfection is necessary for a good measurement of thermal conductivity.

The two ends of the specimen were maintained at different temperatures by two oil baths. These baths were contained in rectangular copper boxes placed about 2.5 cm. apart, and were provided with stuffing boxes through which ran the crystal rods, projecting about 6 cm. into the bath and 10 cm. below the surface. The stuffing boxes were carefully designed so as not to exert an appreciable mechanical stress on the rods, since a mechanical stress at the stuffing boxes, which is the region of rapid change of temperature, would introduce extraneous e.m.f.'s. Both baths were vigorously stirred. One bath was provided with an electric heater with which temperature was varied in the range between room temperature and 100° C. No regulator was used; in changing temperature a heavy heating current was used, and after the desired temperature was reached it was kept very nearly constant by adjusting the heating current to that value which experiment showed was appropriate to that particular temperature. The exact temperature of each bath was read on calibrated thermometers to 0.01°. Since temperature equilibrium was attained between the crystal rods and the bath almost immediately, the error due to drift in the bath temperature was negligible. Readings were made with both ascending and descending temperature; the usual temperatures of the hot end were: room temperature, 40°, 60°, 80°, 100°, 75°, and 55°. The cold end, at the temperature of the cold bath, started at room temperature and gradually increased by conduction through the rod until at the end of the run it was usually about 28°. In order to decrease the total time of the run, the bath was cooled for the decreasing readings by drawing out hot oil and pouring in cold. The total time of a run was about 2 hours.

The thermal e.m.f. measured was that between the crystal rod and commercial copper wire. Connections were made to the crystal rods by soft soldering to each end a copper wire 0.030 cm. in diameter. The identical copper wire was used with all the specimens so that the relative results are not affected by any peculiar properties which this particular copper wire may have had.

It is evident from the dimensions of the rods and the bath that the temperature was perfectly uniform in the neighborhood of the soldered connections, and that therefore a true measure was obtained of the thermal e.m.f. between the crystal and copper.

The thermal e.m.f. was measured by a null method on the same potentiometer which was previously used in measuring the effect of pressure on thermo-electric quality,[6] and it has already been sufficiently described in detail. The thermal e.m.f. of Bi was so large that it was measured with a Siemens and Halske millivoltmeter, which was especially calibrated for this work by a simple method with a standard cell and high resistances.

In calculating the results, the observed e.m.f.'s had to be first corrected for drift of the temperature of the cold end, reducing all readings to a cold end temperature of 20°. This was easily done graphically from the readings at room temperature, 40°, and 60°, the curvature in no case being high enough to introduce perceptible error into the correction. The corrected readings were then plotted on large scale plotting paper, and a smooth curve drawn through the points. In almost all cases the ascending and descending readings agreed within experimental error. This is an important point, and is evidence of freedom from internal changes in the crystal produced by changes of temperature, such as might occur if there were stresses at the stuffing boxes or if there were incipient cleavages. This condition has not been attained in considerable of the work previously done with Bi.

The smooth curve was in all cases within experimental error a curve of the second degree. From these curves two data were now taken, the total e.m.f. of the rod between 20° and 100° (E_0), and the deviation from a linear relation of the observed e.m.f. at the mean temperature of 60° (Δ). These two data are sufficient to determine the two constants of the second degree relation between temperature and e.m.f. For each of the metals E_0 and Δ were now plotted against a parameter determining the orientation of the rod with respect to the crystal axes. In the case of Zn and Bi this parameter was the angle between the basal plane and the length of the rod; in the cases of Sn and Cd it was the specific electrical resistance at 20° C. of the rod, which was especially measured. It has already been explained that for these samples of Sn and Cd the specific resistance gave the most reliable determination of orientation. Through the observed values of E_0 and Δ smooth curves were now passed, and from these smooth curves the values of E_0 and Δ were taken at regular intervals. From these values the corresponding values of Peltier heat and Thomson heat against copper were calculated by well known methods as follows:

The relation between total e.m.f. and temperature is of the form

$$E_{\mathrm{Cu-M}} = a(t - 20) + b(t - 20)^2,$$

where t is temperature in degrees Centigrade. The usual sign convention is employed; a positive E means that current flows from copper to the crystal at the hot junction. Now for the Peltier heat between the metal under investigation and copper we have the familiar thermodynamic relation

$$\begin{aligned} P_{\text{Cu}-\text{M}} &= \tau \frac{dE}{d\tau} \\ &= \tau[a - 40b + 2bt] \\ &= \tau[a' + 2bt] \end{aligned}$$

where τ is absolute Centigrade temperature and $a' = a - 40b$. For the Thomson heat we have

$$\sigma_{\text{M}} - \sigma_{\text{Cu}} = \tau \frac{d^2E}{d\tau^2} = 2b\tau.$$

Now by definition,

$$E_0 = a \cdot 80 + b \cdot \overline{80}^2,$$

and

$$\begin{aligned} \Delta &= \frac{80}{2}[a + b \cdot 80] - [a \cdot 40 + b \cdot \overline{40}^2] \\ &= b\frac{\overline{80}^2}{4}. \end{aligned}$$

These equations, solved for a' and b give

$$a' = \frac{E_0 - 6\Delta}{80}, \qquad b = \frac{4\Delta}{\overline{80}^2}.$$

The values of a' and b calculated in this way were now plotted against the orientation parameter. For the sake of uniformity and for theoretical reasons to be described later, the orientation parameter was in all cases now chosen as the specific resistance. For Zn and Bi the specific resistances were calculated from data given in a previous paper[1] from the location of the cleavage plane. It will be noticed that except for the factor τ, a' and $2b$ are equal to $P_{\text{Cu}-\text{M}}$ and $\sigma_{\text{M}} - \sigma_{\text{Cu}}$ at 0° C.

There now follows the detailed data for the various metals.

Detailed Data.

Zinc. The 8 samples used have already been described under the measurements of thermal conductivity. In Figure 3 are shown the observed e.m.f.'s corrected for the drift of the lower temperature for

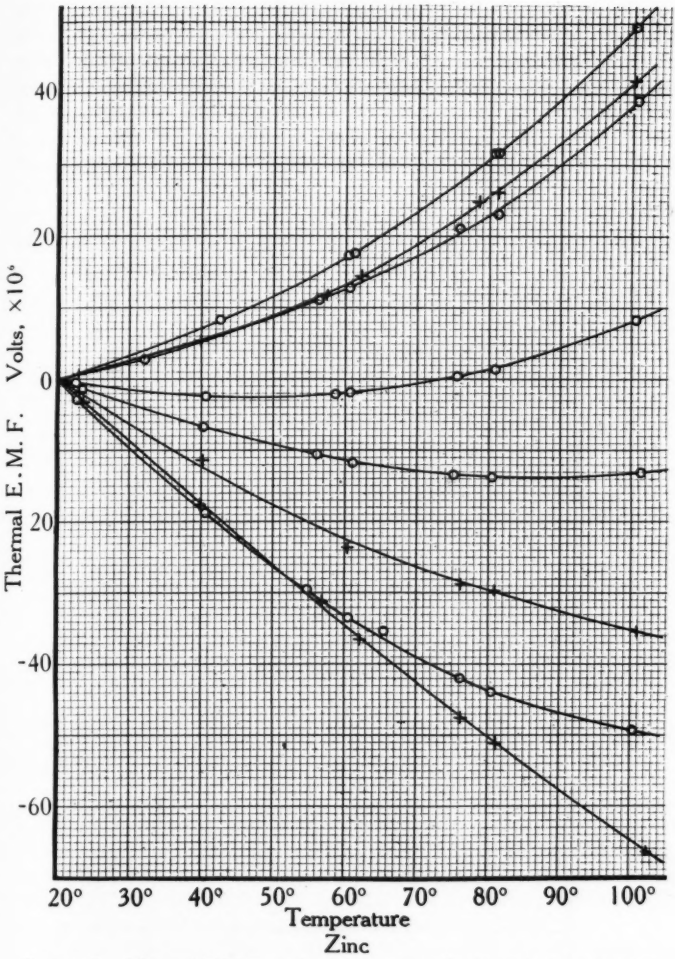

FIGURE 3. Thermal E.M.F. against copper as ordinate against temperature of the hot junction as abscissa for zinc rods of different orientations. Reading from the top down, the axis of the crystal makes the following angles with the axis of the rods: 86.5°, 83°, 80°, 60°, 57°, 48°, 46.5°, 35°.

all the specimens of zinc of various orientations. Notice that the thermal e.m.f. changes sign with the orientation. This series for Zn gives a fair idea of the experimental accuracy reached with the other metals also, and detailed data will not be given for them. The experimental curves for Zn are of the second degree within experimental error. The simplest criterion of this is that at 60° the difference between the actual curve and the straight line connecting the 20° with the 100° point is 4/3 as great as the difference at 40° and 80°. From the family of curves of Figure 3 the values of E_0 and Δ were obtained graphically, and are shown in Figure 4, plotted against the angle between the hexagonal axis and the length of the rod. In Figure 4 are also drawn the smooth curves which seemed to best

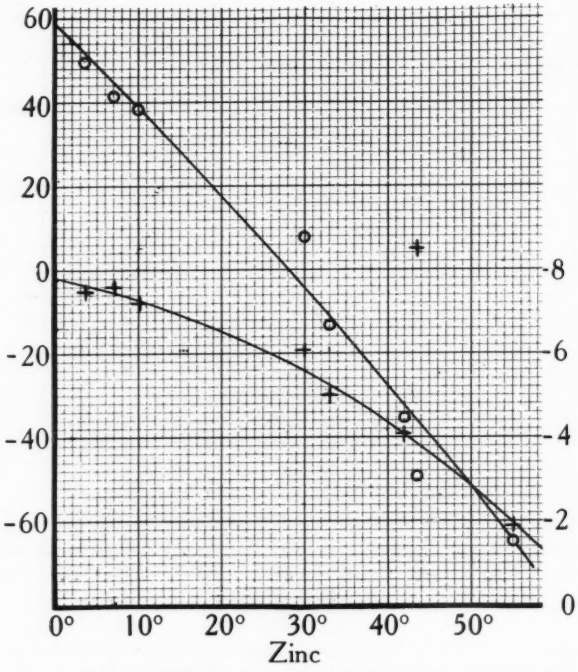

FIGURE 4. Values of E_0 in micro-volts (circles, scale to the left) and Δ in micro-volts (crosses, scale to the right) against the angle between the crystal axis and the length of the rod as abscissa for zinc.

summarize the experimental results. There does not seem to be much question possible as to the best way to draw these curves; only one experimental point is badly off, the value for Δ of the 43.5° specimen. It is of course evident that the percentage error in Δ is much larger than in E_0.

Finally from the smooth curves for E_0 and Δ, the values of a' and b were calculated, and are plotted in Figure 5 against specific resistance.

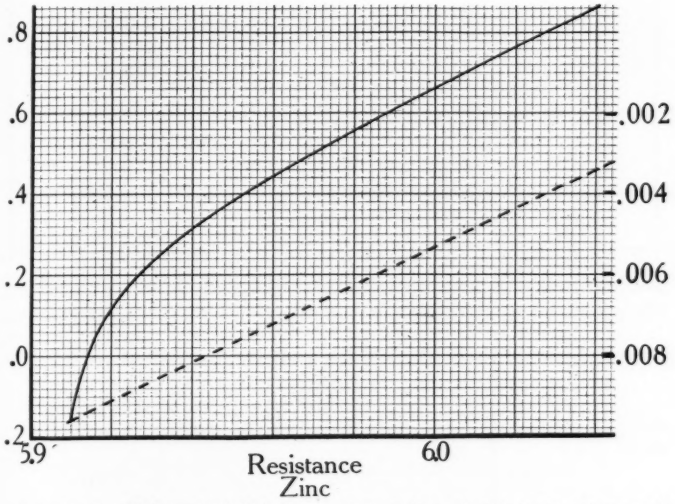

FIGURE 5. Values of a' (full line, scale to left) and of b (dotted line, scale to right) against specific resistance of zinc, a' is closely related to the Peltier heat, and b to the Thomson heat; see equation on page 114.

In computing the specific resistances from the angles of the axis the values $\rho_{11} = 6.13 \times 10^{-6}$ and $\rho_1 = 5.93 \times 10^{-6}$ were used. It appears from Figure 5 that the relation between b and resistance is linear within experimental error, but that the relation between a' and specific resistance cannot well be linear.

Bismuth. 10 rods were used, of the material already described under thermal conductivity, of orientations between the cleavage plane and length varying from 0° to 21.5°. The departure of e.m.f. from linearity with temperature is relatively much less for Bi than for

Zn, so that the value deduced from the curves for Δ is relatively much more uncertain. The following values were found (Table I.). In

TABLE I.

THERMAL E.M.F. DATA FOR BISMUTH.

Angle between Cleavage Plane and Length	Total E.M.F. against Cu 20° to 100°	Departure from Linearity at 60°	Average by Groups		
			Angle	Total E.M.F.	Departure
0°	4460×10^{-6}	50×10^{-6}	0°	4500	25
0°	4540	0			
4.5°	4610	0	5.5°	4610	20
6.5°	4610	40			
10°	5040	80	10°	5040	80
17.5°	5080	100	17.7°	5110	50
18.0°	5150	0			
20.3°	5200	0			
21.5°	4900	100	21.1°	5170	70
21.5°	5420	100			

plotting, rods of nearly the same orientation were grouped together. The results by groups are plotted in Figure 6, with the smooth curves.

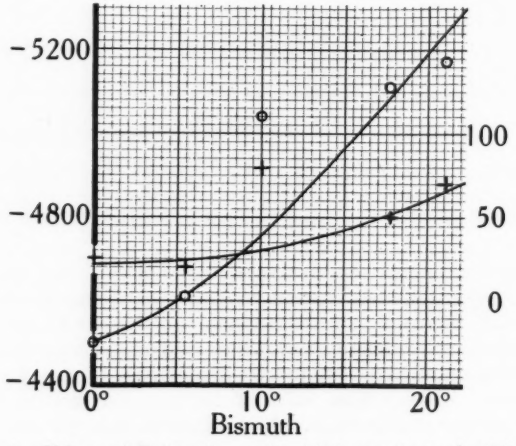

FIGURE 6. Values of E_0 in micro-volts (circles, scale to the left) and Δ in micro-volts (crosses, scale to the right) against the angle between the basal plane and the length of the rod as abscissa for bismuth.

The proper location of the curve for Δ is evidently in much greater doubt than that for E_0.

In Figure 7 are plotted a' and b calculated from these curves at intervals of 0°, 5°, 10°, 16°, and 22°. In converting orientation to specific resistance the values $\rho_\perp = 109 \times 10^{-6}$ and $\rho_{11} = 138 \times 10^{-6}$ were used. Again it is evident that within experimental error b is linear against specific resistance, and a' is probably not linear, although the departure is much less than for *Zn*.

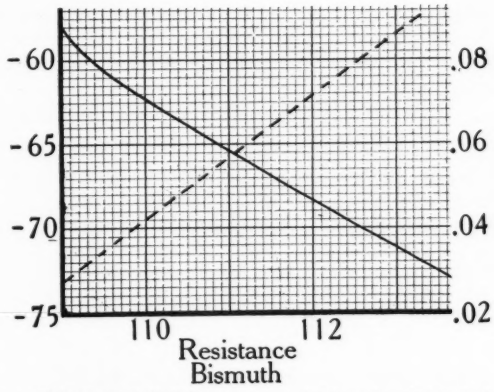

FIGURE 7. Values of a' (full line, scale to left) and of b (dotted line, scale to right) against specific resistance of bismuth. a' is closely related to the Peltier heat, and b to the Thomson heat; see equation on page 114.

Cadmium. 14 rods were used, of which 9 were later selected for the thermal conductivity measurements. These were all of Kahlbaum's best grade of Cd. The specific resistances of these rods were distributed with fair uniformity over the range of values from 6.88 to 8.36×10^{-6}. The values previously found for the specific resistances are: $\rho_\perp = 6.80$, $\rho_{11} = 8.30$, so that practically the entire range of possible orientations was represented here. (The high value 8.36 given above against 8.30, the maximum previously found, deviates no more than single samples sometimes do.)

In calculating the results, there was at first considerable question whether the relation between temperature and e.m.f. was really of the second degree or not. Several of the individual curves differed appreciably from the quadratic form, but the discrepancies were

irregular, sometimes the greater curvature being found at the higher temperature end of the curve, and sometimes at the low temperature end. In order to see whether there was any systematic deviation from the second degree relation, the deviations from linearity of all the curves were found at 40°, 60°, and 80°, and the deviations at each temperature plotted against specific resistance. It was found that the irregularities were unsystematically distributed, so that the best smooth curve through the 40° points was identical within experimental error with that through the 80° points and the ordinates of this curve were ¾ of those of the smooth curve through the 60° points. But this is exactly the condition that the curve be of the second degree. All three of these deviation curves were linear in specific resistance.

In Figure 8 is shown E_0 and Δ as a function of specific resistance

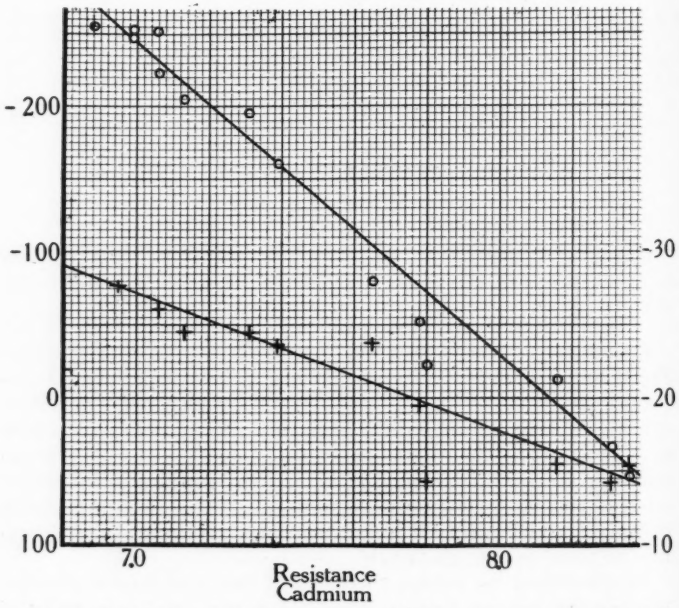

FIGURE 8. Values of E_0 in micro-volts (circles, scale to the left) and Δ in micro-volts (crosses, scale to the right) against the specific resistance in the direction in question as abscissa for cadmium.

(In the curve for Δ several of the values at low specific resistances are averaged into a single point, the values being so nearly coincident that it was not easy to separate them graphically.) In Figure 9 are plotted the values calculated from E_0 and Δ of a' and b. Since E_0

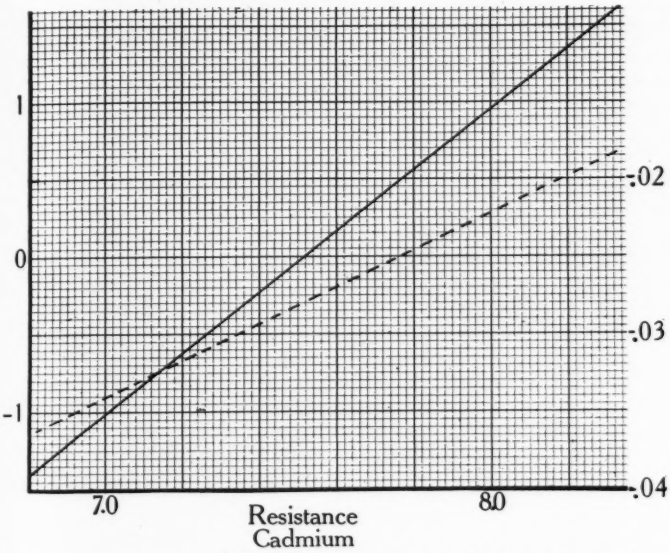

FIGURE 9. Values of a' (full line, scale to left) and of b (dotted line, scale to right) against specific resistance of cadmium. a' is closely related to the Peltier heat, and b to the Thomson heat; see equation on page 114.

and Δ are linear in specific resistance, a' and b must be linear also, so that it was necessary to calculate only two points on each of the curves. Notice that this is the first case yet found of an a' linear with specific resistance.

Tin. 14 rods were used; of these 14 rods, 8 were of Bureau of Standards melting point tin, and 6 were of Kahlbaum's purest grade. No difference whatever could be seen in the behavior of tin from these two sources, and the results obtained with both were averaged indiscriminately. The range of specific resistances of these rods was from 9.89 to 13.23 $\times 10^{-6}$ against 9.9 to 14.3 found previously for

the entire range of orientations. However, the distribution of the rods over the range of orientations was not uniform, tin showing a particular disinclination to crystallize with the basal plane perpendicular to the length. Of the samples used 1 had a specific resistance of 13.23, 3 were between 11.1 and 11.2, 1 was 10.6, and the rest were between 9.9 and 10.3.

The relation between thermal e.m.f. and temperature was much more nearly linear than usual, so that the value of Δ is more in error. In Figure 10 are shown the experimental values of E_0 and Δ against

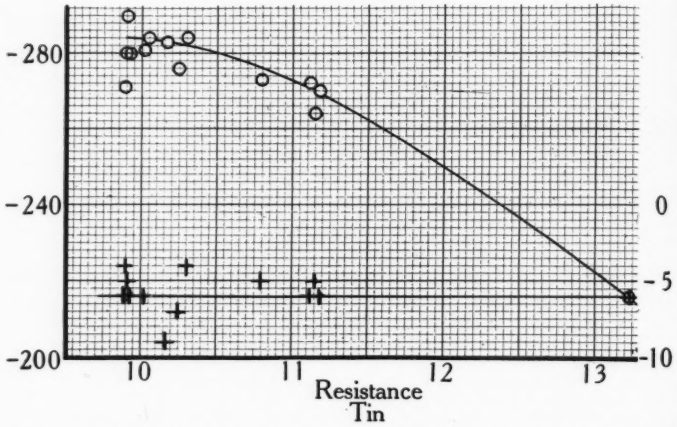

FIGURE 10. Values of E_0 in micro-volts (circles, scale to left) and Δ in micro-volts (crosses, scale to right) against specific resistance in the direction in question for tin.

specific resistance and in Figure 11 the values calculated therefrom for a' and b. Since Δ is constant against specific resistance, it is obvious that b is constant also. Taking as the best value for Δ -6×10^{-6}, the corresponding value of b is -0.0075×10^{-6}.

As in all the other cases, b is linear against specific resistance, but as was also the case with Zn and Bi, a' is not linear within experimental error.

Antimony. Measurements were made on only one specimen of antimony, so that the data are not at hand for a determination of the variation of thermo-electric quality with direction, but since this

measurement was on a single crystal rod, and most previous measurements have been on haphazard aggregates, it seems of interest to record the results.

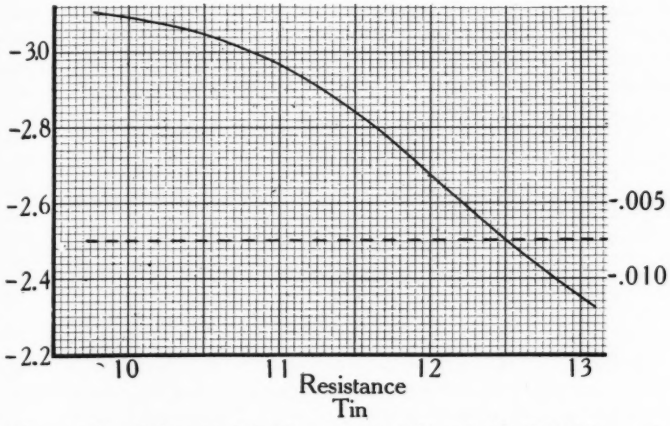

FIGURE 11. Values of a' (full line, scale to left) and of b (dotted line, scale to right) against specific resistance of tin. a' is closely related to the Peltier heat, and b to the Thomson heat; see equation on page 114.

The specimen was of Kahlbaum's purest grade, with the cleavage plane parallel to the length. This was the only one of the specimens investigated for which there was hysteresis between readings with increasing and decreasing temperature of more than the experimental error. The e.m.f.'s with decreasing temperature were about 2.5% lower than those with increasing temperature, the difference therefore being in a direction the reverse of ordinary hysteresis. The mean of the increasing and decreasing readings was used in calculating the results which were as follows:

$$E_0 = +3850 \times 10^{-6} \text{ volts}, \qquad \Delta = +135 \times 10^{-6},$$

whence

$$P_{\text{Cu-Sb}} = \tau[58.25 + .169t] \times 10^{-6}.$$

This is more than twice as high as the value found by Matthiesen[7] for crystalline Sb.

Tellurium. Results, not very satisfactory, were obtained for 3 specimens. The difficulty of making castings which are truly one

grain is even greater than for Bi, and I have not yet attained success. The requirements here are much more exacting than in the previous work because the specimens must be much longer. The specimens investigated here were doubtless not all one grain, but the grains of which they were composed all had very nearly the orientation given. The tellurium used was from the Raritan Copper Works, to whom I am much indebted for specially refining it to remove all selenium. The properties of this Te are reported in greater detail in a previous paper.

The measured e.m.f.'s against temperature are shown in Figure 12. There is no consistent variation of e.m.f. with direction. The curvature is large, corresponding to a Thomson heat much larger than for any of the other metals.

The specific resistance of 2 of the 3 samples was measured; that of the 7° sample was 0.0597 ohms per cm. cube, and that of the 12.5° sample 0.0613.

Theoretical Discussion.

Consider a thermo-couple composed of a straight crystal rod running from a hot region in which the temperature is uniform to a cold region in which the temperature is also uniform. The circuit is to be completed by a copper wire (Figure 13). Then it is a matter of experiment that the e.m.f. of the couple depends only on the terminal temperatures and the orientation of the rod with respect to the crystal, and not at all on how the copper wire is attached at the ends, or on any other modification which may be made in the two regions at constant temperature. In particular, the e.m.f. is the same whether the copper wire is attached as at A to a surface perpendicular to the length of the rod, or whether it is attached as at B to an oblique surface. Within the hot region, heat is absorbed in the one case at the surface A, and in the other case at the surface B, and since the total e.m.f. is the same and no modification has been made in any other part of the circuit, the heat absorbed at the two surfaces A and B must be the same. But if the orientation of the rod with respect to the crystal were changed, the heat absorbed locally at the surface of attachment of the copper wire would in general change, because the total e.m.f. changes with the orientation. Hence it follows that the heat absorbed when a current passes out of a crystal rod into an isotropic medium depends on the direction of flow of the current in the rod, and not on the orientation of the surface by which it leaves (of course it also depends on the nature of the isotropic medium).

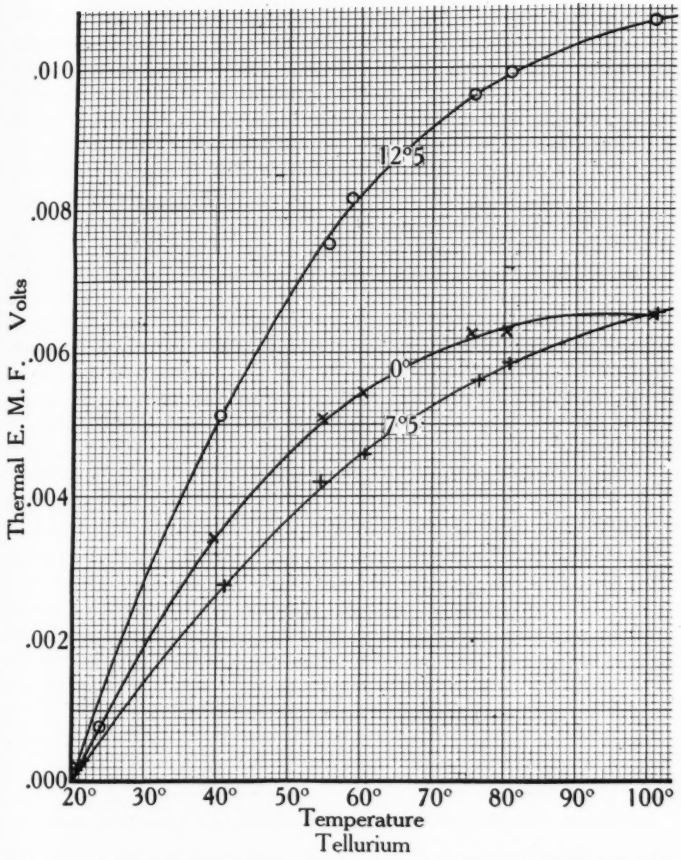

FIGURE 12. Thermal E.M.F. against copper in volts as ordinates plotted against the temperature of the hot junction as abscissa for rods of tellurium of the indicated angles between the crystal axis and the length of the rod.

Let us now suppose that the copper terminal is attached at the end of a right angled arm as shown in Figure 14, the crystalline orientation being uniform throughout the entire specimen. The total e.m.f. is the same as in the first case, because no modification made in

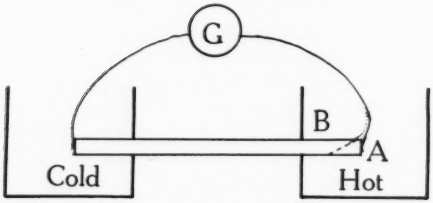

FIGURE 13. Schematical representation of the connections in measuring the thermal E.M.F. of a crystal rod against copper. The E.M.F. is the same whether the crystal rod is cut off perpendicularly as at *A* or obliquely as at *B*.

the region at constant temperature affects the e.m.f., and therefore the total heat absorbed in the hot region is unaltered. But the heat absorbed on leaving the surface *C* is now that appropriate to a flow in the crystal at right angles to the original direction. This is in general different from the original heat. There must therefore be an absorption of heat somewhere else in the hot region, and the principle of sufficient reason suggests that this can be only where the direction of the current flow changes. The amount of heat so absorbed where the direction changes is determined by the requirement that together with the surface heat at *C* it add to the right amount.

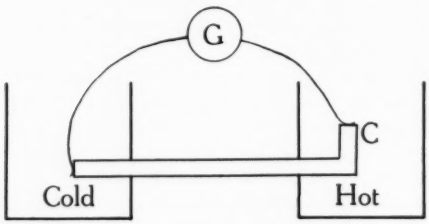

FIGURE 14. The thermal E.M.F. is the same in this figure as in figure 13.

We are thus led to the concept of an internal Peltier heat in a crystal which occurs when the direction of current flow changes at constant temperature. The magnitude of this effect is obviously determined when the ordinary Peltier heat at emergence is known as a function of direction, for it is determined by the simple requirement that the internal Peltier heat on changing from one direction of flow to another is equal to the difference of the emergent Peltier heats for these two directions of flow.

The necessity for the existence of this internal Peltier heat does not seem to have been previously noticed; it is not mentioned by either Voigt or Thomson.[8] The inclusion of it will essentially modify Voigt's analysis. It would seem that the mere existence of this effect should have important consequences on our theoretical views as to the nature of electrical conduction; it is hard to see according to any of the usual pictures why there should be any such effect at all.

For theoretical considerations the dimensions of P are important. P is heat absorbed per coulomb, or it may also be expressed as heat absorbed per electron. This means that the effect cannot be a momentum or a kinetic energy effect arising from a difference of natural velocity of the electrons in different directions in the crystal, for such effects would be proportional to the velocity of each electron, so that the resultant effect per electron would be proportional to the current, and therefore not a constant. In explanation, it almost seems necessary to ascribe to the electron a polar character, and to suppose that in the crystal there are different orienting forces depending on the direction of motion in the crystal. One is reminded of the magnetic doublet character which Compton[9] would ascribe to the electron.

The total e.m.f. in such a circuit as we have been considering is maintained by the Peltier heats at the two ends, and by the Thomson heat in the region where there is a temperature gradient. The relations between the Peltier heats and the Thomson heats for a long slender rod of any orientation with respect to the crystal we assume to be given by the thermodynamic analysis of Thomson, so that for any definite direction we have the relations:

$$P_{\mathrm{Cu-Crys}} = \tau \frac{dE}{d\tau},$$

$$\sigma_{\mathrm{Crys}} - \sigma_{\mathrm{Cu}} = \tau \frac{d^2E}{d\tau^2},$$

where E is the total e.m.f. for the direction considered, and σ is the Thomson heat for current flow in the crystal in that particular direction. Now it seems highly probable that the analysis of Voigt for the heat absorbed internally when the current flow is straight may be accepted without change. Voigt puts the Thomson heat absorbed reversibly equal to the work received by the current in flowing through a Thomson "e.m.f." This Thomson e.m.f. is in nature a vector, and as suggested by the adequacy of the ordinary

thermodynamic analysis for an isotropic substance, we assume it is a linear vector function of the temperature gradient. The coefficients of the linear vector function are the Thomson coefficients of the crystal. Precisely the same symmetry considerations apply to them as to the coefficients of other linear vector functions, for instance, to the electrical resistance in different directions, or to the thermal resistance; the symmetry relations are the same and the manner of variation with direction is the same. In particular, the Thomson coefficients for the crystals considered here belonging to the trigonal, tetragonal, and hexagonal systems have rotational symmetry about the principal axis and the variation with direction is given by the equation

$$\sigma_\theta = \sigma_{11} \cos^2 \theta + \sigma_\perp \sin^2 \theta,$$

where θ is the angle between the direction considered and the principal axis, and σ_{11} and $\sigma_\perp$ are the Thomson coefficients for flow along and at right angles to the axis.

It is a consequence that σ is a linear function of the specific resistance, just as was the reciprocal thermal conductivity.

The Peltier heat at the surface, as well as the internal Peltier heat, was not at all considered by Voigt, so that his formulas cannot be applied without further examination to any actual thermo-couple. (The inadequacy of the analysis of Voigt may be inferred from his formula 433 on page 550, according to which the total heat absorbed in a complete thermo-electric circuit must be zero, so that there is no provision made for the source of the integral e.m.f. around the circuit.) The question that we now have to consider in supplementing Voigt's analysis is what are the necessary symmetry relations on P? The symmetry relations on σ involved essentially the assumption that it was a linear vector function of the temperature gradient. Now P is a function of direction, but there seems to be no natural argument for the symmetry relations of a *general* direction function such as there is for a *vector* function. In particular there would seem to be no reason for expecting P to be a linear function of the direction cosines—why might it not as well be a linear function of the direction tangents? As far as I can see, there is no reason to expect any special manner of variation of P with direction, and in particular no reason at all to expect that P should be the same function of direction as σ. It would follow that the total e.m.f. of a circuit would not necessarily be expected to follow Voigt's formula, and in particular there is no reason to think that the total e.m.f. ought to be a linear function of the resistance.

It does, however, seem natural to expect that P should have rotational symmetry about the principal axis, although I can see no mathematical necessity for such. This is strongly suggested by the experiments. When I made the experiments, I had not examined Voigt's analysis carefully, and expected his results to apply. Therefore in determining the orientation of the crystal rods I determined only the angle between the length of the rod and the principal axis. If P has rotational symmetry, this is adequate. That it is adequate is suggested by the experimental results, since with only a few exceptions, smooth curves are obtained on plotting total e.m.f. against orientation with respect to the axis. If two parameters were required, the curves in one parameter would not be expected to be smooth. In the case of Bi, I have since determined that, in the two specimens whose cleavage planes were parallel to the length, the secondary cleavage planes in one rod made an angle of 66° with the length, and in the other an angle of 81°, with corresponding values for E_0 of 4460 and 4540×10^{-6} volts, which probable differ no more than the experimental error. One may at least draw the conclusion that for these four metals P does not depend importantly on orientation with respect to the secondary crystal axes.

That P does not have the symmetry relations of Voigt has already been brought out in the detailed presentation of data. In all cases the Thomson heat is within experimental error a linear function of electrical resistance, but for Bi, Zn, and Sn, P is not such a function.

An examination of the signs shows that there is no universal relation between heat absorption and the change of direction of flow. Thus for Sn and Bi heat is absorbed when the direction of current flow changes from parallel to perpendicular to the axis, whereas for Zn and Cd heat is given out for the same change of direction.

The fact that thermal e.m.f. varies with direction in a crystal has an interesting bearing on a question which has been much discussed, namely the law of Magnus. This law states that in a circuit composed of a single perfectly homogeneous metal no circuital e.m.f.'s can be generated by any distribution of temperature. It has been claimed a number of times that the law is not true, but the concensus of opinion seems to be that such apparent exceptions are to be explained by lack of perfect homogeneity in the metal. Now it is at once obvious that this law can have no application to a crystal, for high e.m.f.'s may be generated in such circuits as that shown in Figure 15 cut from a single crystal. Now of course all metals of practise are multi-crystalline, the grains being presumably oriented at haphazard.

Experiments made on a large scale would be expected to verify the law of Magnus, but when any part of the circuit becomes so small that the individual crystals are comparable in size with the cross section of the circuit, one might expect these characteristically crystalline properties to produce an appreciable net effect, and the law of Magnus to fail. It is not quite evident from the experimental evidence now in hand whether to expect such small scale effects with metals crystallizing in the cubic system. If the Peltier heat satisfies the same symmetry relations in a cubic crystal as does the Thomson Heat, then we should not expect such an effect, but we have seen that there seems to be no simple necessary connection between P and direction, so that we need not expect P necessarily to have spherical symmetry

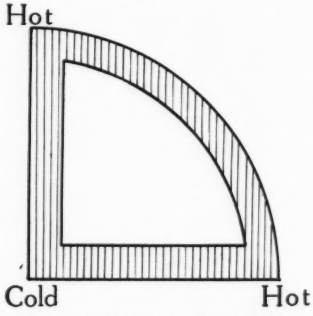

FIGURE 15. To illustrate conditions under which current may flow in an unequally heated circuit cut from a single crystal. If the materials were amorphous, no current would flow.

in a cubic crystal. If P has not spherical symmetry, it need not average to zero when the cross section of the circuit is composed of comparatively few grains. Entirely apart, however, from these crystalline effects, there is the consideration that non-uniform temperature gradients cannot be maintained in a solid without producing mechanical stresses, and so making the material non-homogeneous.

It seems then that interest in the law of Magnus is reduced to a somewhat academic position. It is a result of experiment that any such effects are small, but under properly chosen conditions of experiment we may expect such effects to be found. Two interesting questions remain, however: does the law of Magnus hold for a liquid metal such as mercury? And in a single crystal rod, in which there is a

uniform temperature gradient and no mechanical stress, is the Thomson heat absorbed by the current a function only of the temperature difference between two points and not a function of the temperature gradient?

Average Values. There are no previous results on single crystals to compare with these (except for Bi), but it is natural to expect that previous results on polycrystalline metals should agree with some sort of an average, throughout the crystal, of the results found here. The theoretical discussion indicates what sort of agreement to expect. The Thomson heat satisfies the symmetry relations of Voigt, so that his value for the average should apply. The Peltier heat seems to have no such symmetry relations, so that Voigt's expression for the average does not apply, but we expect, nevertheless, an agreement as to sign and order of magnitude between the observed P, for polycrystalline metals, and the average calculated for the crystal by Voigt's formula.

In Table II. are collected the values for P and σ at 0° C. against copper taken from my previous paper on extruded wires,[6] and the values for P and σ in different directions of the crystals of this paper. In the case of Bi, which has a very large P, there is agreement in both sign and order of magnitude. σ is also of the right sign, but when averaged by Voigt's formula over all directions in the crystal it is evident that σ for the crystal will be much larger than for the extruded wire. But it must be remembered that there is considerable error possible in the σ given for the crystal, and it is also possible that in the extruded wire all orientations were not uniformly represented, so that one cannot be perfectly sure that the data for Bi are inconsistent with some sort of average law. But the other metals seem to make this impossible. Both P and σ for all directions in Sn have the wrong sign to agree with previous values for Sn wire. Cd crystals have the wrong sign for σ and a value for P also of the wrong sign and at least 10 fold too small numerically. With Zn it is not impossible that some sort of an average of the P of the crystal should agree with the P of the wire; σ furthermore has the right sign, but the average for the crystal is about 4 times too small. One may try to improve the agreement, on remembering that the copper of these experiments may have been different from that used previously, by correcting the values given for the extruded wire by a constant additive correction applied to all the P's, and another additive correction to all the σ's. But a little trial will show that this is not possible; a change that improves the agreement in one place makes it worse in another.

TABLE II.

COMPARISON OF THE THERMAL E.M.F. AGAINST Cu OF ISOTROPIC AND UNICRYSTALLINE METALS.

Metal	Isotropic		Unicrystalline		
	Peltier Heat at 0° C Against Cu.	Thomson Heat at 0° C Against Cu.	Specific Resis.	Peltier Heat at 0° C Against Cu.	Thomson Heat at 0° C Against Cu.
Sn	$-2.547\times10^{-6}\tau$	$-.0110\times10^{-6}\tau$	9.9×10^{-6} 13.0	$3.10\times10^{-6}\tau$ 2.35	$.0075\times10^{-6}\tau$ .0075
Cd	9.225	.227	6.8 8.3	—1.41 +1.54	—.036 —.019
Zn	.270	—.0196	5.910 6.039	— .147 + .854	—.0097 —.0035
Bi	—77.20	.0223	109 113	—57.8 —71.5	.0275 .0875

The conclusion seems to be forced that the thermo-electric properties of a polycrystalline aggregate (at least of non-cubic metals) cannot be computed from the average of the properties of a single crystal in the same way that the electrical resistance or the thermal conductivity can be calculated. In explanation it is to be noticed that, in any polycrystalline aggregate of non-cubic metals formed in the usual way by casting, there must be intense internal stresses, because of the unequal thermal expansion of the grains in different directions, and that thermo-electric properties are much more sensitive to such stresses than resistance or thermal conductivity. If this is correct, one will in the future attach less theoretical significance than hitherto to thermo-electric properties measured on polycrystalline aggregates of these metals.

SUMMARY.

1. Thermal Conductivity. The thermal conductivity of Bi, Zn, Cd, and Sn is measured at room temperature for different directions in the crystal. It is found that Voigt's symmetry relations are satisfied in that in any single crystal the reciprocal of thermal conductivity varies linearly with electrical resistance as the orientation changes. The generalized Wiedemann-Franz law, however, does not hold for all directions in a crystal in that the ratio of thermal to electrical conductivity is in general a function of the orientation. Within experimental error it is not impossible that the Wiedemann-Franz ratio is constant for Bi and Sn, but in Zn the thermal conductivity varies more rapidly with direction than does the electrical conductivity, and Cd the variation of thermal conductivity is less rapid.

2. Thermal E.M.F. The thermal e.m.f. against copper is measured between 20° and 100° C. as a function of direction in the crystal for Bi, Zn, Cd, and Sn, and isolated results are also found for Sb and Te. In general the thermo-electric force varies greatly with direction. From the thermal e.m.f. data the Peltier and the Thomson heats are calculated. Voigt's symmetry relations are shown to be satisfied by the Thomson heat, which is a linear function of electrical resistance. The Peltier heat, on the other hand, was apparently not considered in Voigt's analysis, and these experiments show that the symmetry relations to which it is subject are not the same as those for the Thomson heat. It is probable that the Peltier heat has rotational symmetry about the principal crystal axis, but there appears to be no necessary restriction as to its variation in directions inclined to the axis. It is pointed out that the Peltier heat depends only on the

direction of current flow within the crystal just before emergence, and not on the orientation of the surface through which it emerges. It is a consequence that there is an internal Peltier heat, i. e., a reversible absorption or generation of heat where the direction of current flow changes within the crystal. The mere existence of this effect should be most important for theories of electrical conduction. It is also a consequence of the difference of thermal properties of a crystal in different directions that the generalized law of Magnus cannot hold for a crystal, but in general thermal currents will flow in an unequally heated closed circuit cut from a single crystal. Finally, the thermoelective properties of an ordinary polycrystalline aggregate of non-cubic crystals cannot be found by averaging the properties of the single crystals in different directions.

It is a pleasure to acknowledge the assistance received from Mr. E. T. Lane in making nearly all the readings of thermal e.m.f. It is also a pleasure to acknowledge financial assistance received from the Rumford Fund of the American Academy.

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